

We claim:

1. A method for enhancing the stability of a solids-stabilized water-in-oil emulsion, said method comprising the step of pretreating at least a portion of
5 said oil prior to emulsification, said pretreating step comprising at least one of the steps of adding dilute acid to said oil, adding a lignosulfonate to said oil, sulfonating said oil, thermally treating said oil in an inert environment and thermally oxidizing said oil.
2. The method of claim 1, wherein said pretreating step comprises adding dilute
10 acid to at least a portion of said oil prior to emulsification, said dilute acid selected from the group consisting of mineral acids, organic acids, mixtures of at least two mineral acids, mixtures of at least two organic acids, and mixtures of at least one mineral acid and at least one organic acid.
3. The method of claim 2, wherein said acid is added to said oil at a rate of from
15 about 8 parts per million to about 30,000 parts per million.
4. The method of claim 2, wherein said method further comprises the steps of determining the pH of said water-in-oil emulsion following emulsification and if necessary adjusting said pH so that it falls in the range of from about 5.0 to about 7.0.
- 20 5. The method of claim 4, wherein said pH of said water-in-oil emulsion is adjusted by adding ammonium hydroxide to said emulsion.
6. The method of claim 1, wherein said pretreating step comprises sulfonating at least a portion of said oil prior to emulsification.
7. The method of claim 6, wherein said step of sulfonating said oil comprises the
25 addition of at least one sulfonating agent to said oil.
8. The method of claim 7, wherein said sulfonating agent is added to said oil at a rate of between about 0.5wt% to about 5wt%.

9. The method of claim 1, wherein said pretreating step comprises adding a lignosulfonate additive to at least a portion of said oil prior to emulsification.
10. The method of claim 9, wherein said lignosulfonate additive is added to said oil at a rate of between about 500 parts per million to about 5000 parts per million.
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11. The method of claim 9 wherein said lignosulfonate additive is oil soluble.
12. The method of claim 9 wherein said lignosulfonate additive is water soluble.
13. The method of claim 1, wherein said pretreating step comprises thermally oxidizing at least a portion of said oil prior to emulsification.
- 10 14. The method of claim 13, wherein said thermal oxidation step is at a temperature of between about 110°C to about 180°C.
15. The method of claim 13, wherein said thermal oxidization step is enhanced by addition of a catalyst.
16. The method of claim 1, wherein said pretreatment step comprises thermally
15 treating at least a portion of said oil in an inert environment prior to emulsification.
17. The method of claim 16, wherein said thermal treatment step is at a temperature in a range of between about 250°C to about 450 °C.
18. The method of claim 16, wherein said thermal treatment step is at a pressure in
20 the range of between about 30 psi to about 300 psi.
19. The method of claim 16, further comprising the addition of dilute acid to said oil prior to emulsification, said dilute acid selected from the group consisting of mineral acids, organic acids, mixtures of at least two mineral acids, mixtures of at least two organic acids, and mixtures of at least one mineral acid and at least
25 one organic acid.

20. The method of claim 16, further comprising the addition of a lignosulfonate additive to said oil prior to emulsification.
21. The method of claim 16, wherein said pretreatment step reduces the viscosity of said solids-stabilized water-in-oil emulsion.
- 5 22. A method for recovering hydrocarbons from a subterranean formation, said method comprising the steps of:
- a) preparing a solids-stabilized water-in-oil emulsion by
 - (1) pretreating at least a portion of said oil prior to emulsification, said pretreating step comprising at least one of the steps of adding dilute
10 acid to said oil, adding a lignosulfonate additive to said oil, sulfonating said oil, thermally treating said oil in an inert environment and thermally oxidizing said oil;
 - (2) adding solid particles to said oil prior to emulsification; and
 - (3) adding water and mixing until said solids-stabilized water-in-oil
15 emulsion is formed;
 - b) injecting said solids-stabilized water-in-oil emulsion into said subterranean formation; and
 - c) recovering hydrocarbons from said subterranean formation.
23. The method of claim 22, wherein said solids-stabilized water-in-oil emulsion is
20 used as a drive fluid to displace hydrocarbons in said subterranean formation.
24. The method of claim 22, wherein said solids-stabilized water-in-oil emulsion is used as a barrier fluid to divert the flow of hydrocarbons in said subterranean formation.
25. The method of claim 22, wherein said pretreating step comprises adding dilute
25 acid to at least a portion of said oil prior to emulsification, said dilute acid selected from the group consisting of mineral acids, organic acids, mixtures of at least two mineral acids, mixtures of at least two organic acids, and mixtures of at least one mineral acid and at least one organic acid.

- 26 The method of claim 25, wherein said solid particles are hydrophobic solid particles.
- 27 The method of claim 25, wherein said dilute acid is added at a treat rate of between about 8 parts per million to about 30,000 parts per million.
- 5 28 The method of claim 25, further comprising the steps of determining the pH of said water-in-oil emulsion following emulsification, and if necessary adjusting said pH so that it falls in the range of from about 5.0 to about 7.0.
- 29 The method of claim 28, wherein said pH of said water-in-oil emulsion is adjusted by adding ammonium hydroxide to said emulsion.
- 10 30 The method of claim 25, wherein said step of adding solid particles to said oil occurs after said step of adding dilute acid to said oil.
- 31 The method of claim 25, wherein said step of adding solid particles to said oil occurs before said step of adding said dilute acid to said oil.
- 32 The method of claim 25, wherein said solid particles are added at a treat rate of
15 about .05 wt% to about 0.25 wt% based on the weight of the oil.
- 33 The method of claim 22, wherein said pretreating step comprises sulfonating at least a portion of said oil prior to emulsification.
- 34 The method of claim 33, wherein said step of sulfonating said portion of oil comprises the addition of at least one sulfonating agent to said oil.
- 20 35 The method of claim 34, wherein said sulfonating agent is sulfuric acid.
- 36 The method of claim 34, wherein said sulfonating agent is added to said oil at a treat rate of from about 0.5wt% to about 5wt%.
- 37 The method of claim 33, wherein said solid particles comprise hydrophobic solid particles.

- 38 The method of claim 33, wherein said solid particles comprise functionalized
asphalts.
- 39 The method of claim 33, wherein said solid particles comprise unfunctionalized
asphalts.
- 5 40 The method of claim 33, wherein said step of adding solid particles to said oil
occurs after said sulfonation step.
- 41 The method of claim 33, wherein said step of adding solid particles to said oil
occurs before said sulfonation step.
- 42 The method of claim 33, wherein said solid particles are added at a treat rate of
10 about .05 wt% to about 2.0 wt% based on the weight of the oil.
- 43 The method of claim 22, wherein said pretreating step comprises adding a
lignosulfonate additive to at least a portion of said oil prior to emulsification.
- 44 The method of claim 43, wherein said lignosulfonate additive is added to said
oil at a treat rate of between about 500 parts per million to about 5000 parts
15 per million.
- 45 The method of claim 43, wherein said solid particles comprise hydrophobic
solid particles.
- 46 The method of claim 45, wherein said lignosulfonate additive comprises at least
one water soluble lignosulfonate additive.
- 20 47 The method of claim 43, wherein said solid particles comprise hydrophilic solid
particles.
- 48 The method of claim 47, wherein said lignosulfonate additive comprises at least
one oil soluble lignosulfonate additive.
- 49 The method of claim 43, wherein said step of adding solid particles to said oil
25 occurs before said step of adding said lignosulfonate additive to said oil.

- .50. The method of claim 43, wherein said step of adding solid particles to said oil occurs after said step of adding said lignosulfonate additive to said oil.
- 51 The method of claim 43, wherein said solid particles are combined with said lignosulfonate additive, and then said combination is added to said oil before
5 said emulsification.
- 52 The method of claim 43, wherein said solid particles are added at a treat rate of about .05 wt% to about 0.25 wt% based on the weight of the oil.
- 53 The method of claim 22, wherein said pretreating step comprises thermally oxidizing at least a portion of said oil prior to emulsification.
- 10 54 The method of claim 53, wherein said oil is thermally oxidized at a temperature of between about 110°C to about 180 °C.
- 55 The method of claim 53, wherein said thermal oxidation step is enhanced by addition of a catalyst.
- 56 The method of claim 53, wherein said solid particles are hydrophobic solid
15 particles.
- 57 The method of claim 53, wherein said solid particles are hydrophilic solid particles.
58. The method of claim 53, wherein said solid particles are bentonite clay.
- 59 The method of claim 53, wherein said solid particles are added to said oil
20 before said thermal oxidation step.
- 60 The method of claim 53, wherein said solid particles are added to said oil after said thermal oxidation step, and before said emulsification.
- 61 The method of claim 53, wherein said solid particles are added as a gel comprised of solid particles and water.

62. The method of claim 61, wherein said solid particles comprise about 1.0 wt% to about 30 wt% of said gel based on the weight said water.
63. The method of claim 61, wherein said gel is added to said oil in a treat range of about 5 wt% to about 95 wt% of said gel to said oil.
- 5 64. The method of claim 53, wherein said solid particles are added to said oil at a treat rate of between about .05 wt% to about 5 wt% based on the weight of the oil.
- 65 The method of claim 22, wherein said pretreatment step comprises thermally treating at least a portion of said oil in an inert environment prior to emulsification.
- 10 66 The method of claim 65, wherein said oil is thermally treated at a temperature in the range of between about 250°C to about 450 °C.
67. The method of claim 65, wherein said oil is treated at a pressure in the range of between about 30 psi to about 300 psi.
- 15 68 The method of claim 65, wherein said solid particles are hydrophobic solid particles.
- 69 The method of claim 65, wherein said solid particles are added to said oil before said thermal treatment step, and before said emulsification.
- 70 The method of claim 65, wherein said solid particles are added to said oil after said thermal treatment step, and before said emulsification.
- 20 71 The method of claim 65, wherein said solid particles are added at a treat rate of about .05 wt% to about 0.25 wt% based on the weight of the oil.
- 72 The method of claim 65, wherein said step of thermally treating said oil further comprises the addition of dilute acid to said oil prior to emulsification, said dilute acid selected from the group consisting of mineral acids, organic acids,
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mixtures of at least two mineral acids, mixtures of at least two organic acids, and mixtures of at least one mineral acid and at least one organic acid.

73. The method of claim 65, wherein said step of thermally treating said oil further comprises the addition of a lignosulfonate additive to said oil prior to emulsification.
74. The method of claim 65, said method further comprising the step of aging said solids-stabilized water-in-oil emulsion following emulsification whereby the viscosity of said emulsion is reduced.
75. The method of claim 74, wherein said step of aging said emulsion comprises centrifuging said emulsion at about 500 rpm to about 10,000 rpm for about 15 minutes to about 2 hours.
76. The method of claim 75, wherein said step of centrifuging said emulsion is repeated.
77. A solids-stabilized water-in-oil emulsion for use in recovering hydrocarbons from a subterranean formation, said emulsion comprising
- (a) oil, wherein at least a portion of said oil is pretreated by at least one of the steps of adding dilute acid to said oil, adding a lignosulfonate additive to said oil, sulfonating said oil, thermally treating said oil in an inert environment and thermally oxidizing said oil;
 - (b) water droplets suspended in said oil; and
 - (c) solid particles which are insoluble in said oil and said water at the conditions of said subterranean formation.